

Variable, self-regulating permeate recycling in organophilic nanofiltration

The present invention relates to an improvement in terms of control and process technology for a method of continuous removal of a component from a liquid mixture using a membrane unit comprising at least one membrane stage. The improvement is that at least some of the overall permeate stream obtained is recycled to the feed vessel and/or beyond the feed vessel but upstream of the conveying device. The presently disclosed method can especially be used for separation of a homogeneously dissolved catalyst from a liquid reaction mixture.

Membrane separation methods, for example for the separation of homogeneously dissolved catalysts from the reaction mixture, are known in principle in the prior art. Reference is made here by way of example to WO 2014/131623 A1.

For membrane separation methods of this kind, improvements in control technology have already been described. International application WO 2014/183952 A1 discloses, for example, a membrane separation method for separation of a homogeneously dissolved catalyst from a reaction mixture, in which two control parameters, the retentate volume flow rate of the membrane separation unit and the retention of the membrane separation unit, are kept constant in order to compensate for fluctuating operating conditions, especially fluctuations in the volume flow rate of the reaction mixture coming from the reaction zone.

In order to keep the aforementioned controlled variables constant, WO 2014/183952 A1 proposes a flow resistor for adjusting the retentate volume flow rate, or keeping it constant, and closed-loop control of the temperature and/or of the pressure in the overflow circuit for adjusting the retention, or keeping it constant.

A problem with the method proposed therein is that it is not productive for all methods to keep the retention of the membrane separation unit constant; instead – taking account of the plant throughput and the membrane area already installed in the membrane separation unit – what is required is optimization, frequently maximization, of the retention of the membrane separation unit during the method. Closed-loop control by means of a flow resistor as described in WO 2014/183952 A1 may possibly have the effect that the membrane area already installed is operated not at the optimal transmembrane pressure but below it. The method described therein can additionally have the effect that, for a given total throughput of the plant and the resulting permeate stream removed therefrom (portion of the permeate stream conducted out of the membrane separation unit on the permeate side), the total permeate stream and the resulting recycled permeate stream on the basis of a simple mass balance taking account of the permeate stream removed (portion of the total permeate stream which is recycled into the membrane separation unit) is smaller than possible and/or would be desirable.

A further disadvantage of the method described in WO 2014/183952 A1 is that it envisages both a vessel for the permeate and a pump in order to obtain a closed-loop control system which is constant on the permeate side. The provision of a pump that pumps permeate from the permeate
 5 vessel into the overflow circuit or the feed vessel, however, is associated with an elevated plant inventory and costs, for example for procurement or for operation, maintenance and repair, which can additionally also result in a plant shutdown and hence production shutdown.

In addition, the installation of a vessel generally has the effect that the portion of the membrane
 10 separation stage on the permeate side is not filled hydraulically, which can possibly lead to elevated safety risks, especially when toxic fluids are used. Moreover, a vessel on the permeate side in addition to the feed vessel gives rise to the possibility that the closed-loop control of the two vessel states may lead to opposite fluctuations.

The problem addressed by the present invention was therefore that of providing a less expensive
 15 method of continuously separating a component from a mixture, preferably for continuous separation of a homogeneous catalyst from a reaction mixture. A further problem addressed by the present invention was that of providing self-regulating permeate recycling in the method of continuous separation of a component from a mixture, preferably of continuous separation of a
 20 homogeneous catalyst from the reaction mixture, in which the membrane area installed can be utilized optimally in different load states, for example for maximization of the retention or yield.

The underlying problem was solved by the method according to Claim 1. Preferred configurations
 25 and embodiments are specified in the subsidiary claims.

The method according to the invention is a method of continuously separating a component from a liquid mixture using a membrane unit which comprises at least one membrane stage and is fed with the mixture as feed,

30 wherein a membrane stage consists at least of a conveying device, one or more membrane module(s) and a feed vessel upstream of the conveying device, and wherein the mixture is guided from the feed vessel by means of the conveying device as feed to the one or more membrane modules, which results in reduction of the component to be separated off, based in each case on the mixture guided to the respective membrane module, in the resulting permeate stream from this
 35 particular membrane module and enrichment in the resulting retentate stream from this particular membrane module or vice versa, characterized in that

the overall permeate stream obtained from the last membrane stage is divided and a portion of the overall permeate stream, the recycled permeate, is recycled to the feed vessel and/or beyond the

feed vessel but upstream of the conveying device and the other portion of the overall permeate stream, the permeate removed, is conducted out of the last membrane stage and out of the membrane unit on the permeate side, wherein the recycling of the recycled permeate to the feed vessel and/or beyond the feed vessel but upstream of the conveying device is effected not by
5 means of a conveying device but by hydraulic means, i.e. by means of a pressure differential that exists between the permeate side of the membrane unit and the suction side of the conveying device or the feed vessel.

In the context of the present invention, what is meant by the term "component to be separated off"
10 is the component intended to permeate through the membrane to a lesser degree in terms of its proportion and/or according to permeability, i.e. the component that is retained by the membrane. The component to be separated off thus has positive retention for the particular membrane modules in question. The component to be separated off may additionally be a single specific chemical substance or else a group of chemical substances that can be considered in a common
15 context for process technology purposes.

"Membrane unit" in the context of the present invention relates to the entire membrane unit supplied with the liquid mixture containing the component to be separated off. A membrane unit consists of at least one membrane stage. Downstream further processing or purification steps and
20 any storage of the permeate removed in a vessel are therefore not part of the membrane unit by definition.

The term "membrane stage" means at least a portion of the membrane unit and includes at least one conveying device, for example a pump, and one or more membrane module(s). If there is just
25 a single membrane stage, the terms "membrane unit" and "membrane stage" should be understood synonymously. The membrane stage has a feed vessel connected upstream of the conveying device, into which the liquid mixture, for example the output from a homogeneously catalysed reaction, is introduced, and from which it is guided to the one or more membrane elements. The permeate recycled can likewise be guided into the feed vessel. Additionally or
30 alternatively, it is possible that the permeate recycled is guided not into the feed vessel, but rather beyond the feed vessel but upstream of the conveying device, i.e. at a point in the conduit between feed vessel and conveying device.

The term "membrane module" utilized for description of the present invention relates to a subunit,
35 in terms of plant technology, of the membrane stage. A membrane module is accordingly an interconnection of one or more membrane element(s). Membrane modules may be configured either as a membrane loop or as a membrane rack. A membrane loop is understood to mean a sub unit in which there is at least one membrane element and at least one conveying device present by which a moving overflow circulation is generated. The term "membrane rack", by contrast, means a

subunit having the features that there is at least one membrane element but no conveying device, and accordingly no moving overflow circulation is generated either.

5 The term "membrane element" in the context of the present invention means the membrane or the structure or the apparatus containing the membrane, and where the desired separation of matter actually takes place, i.e. the component is separated from the mixture or the homogeneous catalyst from the reaction solution. These may be, for example, spiral-wound elements as used in many applications in industrial membrane separation.

10 The basis of the invention is that only the overall permeate stream from the last membrane stage is divided into the permeate recycled and the permeate removed. Should there be only one membrane stage, this single membrane stage is also the last membrane stage. If there are two or more membrane stages, no division takes place in the or in the first membrane stage; instead, the entire permeate stream is guided to the next membrane stage in its entirety. The division is then
15 effected, as described above, exclusively in the last membrane stage. The term "division" in the context of the present invention relates exclusively to the amount or mass flow rate of the overall permeate and means explicitly no additional separation step in which the further components are removed from the overall permeate, i.e., for example, no distillation, no extraction, no crystallization and no further membrane separation steps.

20 One advantage of the method according to the invention is that a portion of the overall permeate stream from the last membrane stage, i.e. the permeate recycled, does not leave the membrane stage and/or does not leave the membrane unit and then is not first recycled via a permeate vessel, for example, but rather remains within the at least one membrane stage and/or the
25 membrane unit and thence is recycled to the feed vessel and/or beyond the feed vessel but upstream of the conveying device. This makes it possible to dispense with a downstream pump that pumps the permeate back into the overflow circuit or back into the feed vessel, since the permeate recycling is self-regulating according to the load. The recycling of the recycled permeate to the feed vessel and/or beyond the feed vessel but upstream of the conveying device is thus
30 effected not by means of a conveying device but rather by hydraulic means, i.e. by means of a pressure differential existing between the permeate side of the membrane unit and the suction side of the conveying device or the feed vessel. In other words: there is no further conveying device, in particular no pump, between the permeate side and the feed vessel.

35 In order to control the exit flow rates of the permeate recycled and the permeate removed, there may be at least one adjustable flow resistor on the permeate side, by means of which the mass flow rate of the permeate is controlled. A flow resistor in the context of the present invention is an actuator with which the mass flow rate of a stream can be controlled, for example a valve. Preference is further given to an embodiment in which there are at least two adjustable flow

resistors, preferably exactly two adjustable flow resistors, on the permeate side, which means that the mass flow rate of the permeate removed and the permeate pressure, especially of the collecting rail, can be adjusted. The flow resistors are especially valves.

- 5 The portion of the overall permeate stream from the last membrane stage which is removed from the membrane stage on the permeate side and from the membrane unit, i.e. the permeate removed, can be guided to a downstream process step. The term "process step" in the context of the present invention may be understood to mean any downstream process, for example further processing or purification process steps or combinations thereof. This especially includes a
- 10 (further) reaction of the component removed, purification by known methods such as distillation, evaporation or the like. Downstream dispensing or transport process steps are also possible. Before the downstream process step, prior storage in a suitable vessel is also possible, for example in a permeate vessel. If there is a permeate vessel, the division of the overall permeate according to the invention is effected upstream of the permeate vessel, such that only the
- 15 permeate removed gets into the permeate vessel. It will be apparent that multiple process steps, optionally via prior storage, may also be effected in succession, for example a purification followed by a conversion of the purified component and additional purification of the reaction product.

With regard to the membrane separation method according to the invention, there is a stable

20 external mass balance, meaning that the mass flow rate of the feed supply to the membrane unit corresponds to the mass flow rates of the permeate streams and/or retentate streams conducted out of the membrane unit. It is possible to make use of this circumstance. In a preferred embodiment of the present invention, the mass flow rate of one stream of the three streams selected from feed to the membrane unit, the permeate removed, and the retentate from the

25 membrane unit is applied to a preceding or downstream process step, and one further stream of the three is controlled toward a target value, for example a constant retentate flow rate, a constant ratio of feed to retentate, etc. On account of the external mass balance, this also results in the third of the three streams mentioned. The scale and hence the absolute mass flow rates are adjustable largely as desired with reference to the membrane module size and number of membrane

30 modules. In a preferred embodiment, the ratio of the retentate mass flow rate that the mass flow rate is 1% to 99%, preferably 10% to 90% and more preferably 15% to 80%. In a further preferred embodiment, the ratio of the mass flow rate of the permeate removed to the overall permeate mass flow rate is 1% to 99%, preferably 30% to 98%, more preferably 60% to 97%. "Process step" in the context of the present invention is a plant or process unit, for example an upstream or downstream

35 chemical reaction in which the permeate/retentate is used, a further separation step, for example a thermal separation such as thin-film evaporation or distillation, or logistics, i.e. especially an upstream or downstream tank farm or a dispensing operation. Upstream process steps are especially continuously performed process steps by means of which a liquid mixture is provided continuously for the present membrane separation process. These are preferably continuously

performed chemical reactions, for example hydroformylation or alkoxycarbonylation, which are elucidated in detail hereinafter.

5 In addition, more particularly, there is also a stable internal mass balance (mass flow rate of the overall permeate, corresponding to the sum total of the mass flow rates of the permeate recycled and the permeate removed). According to the present invention, the internal mass balance is preferably largely independent of the external mass balance, meaning that the outer mass balance is in principle merely the lower limit for the internal mass balance. It is therefore preferable in accordance with the invention that the mass flow rate of the permeate recycled can fluctuate and is established depending, preferably directly depending, i.e. without any permeate vessel in between, on the mass flow rate of the permeate removed. This also means that the mass flow rate of the overall permeate, disregarding technical limitations (resulting from pumps, flow resistors, membrane area, etc.), can be controlled independently of the abovementioned external mass balance, provided that the mass flow rate of the overall permeate is greater than the mass flow rate of the permeate removed.

20 The mass flow rate of the overall permeate depends here on various parameters, for example the temperature (of the membrane module) or the concentration of the components in the mixture. In a preferred embodiment of the present invention, therefore, the pressure on the retentate side and/or the pressure on the permeate side or the resulting transmembrane pressure (TMP = pressure differential between permeate side and retentate side) and optionally the membrane module temperature are controlled in order to optimize the amount of the overall permeate stream or to obtain a desired amount of the overall permeate stream.

25 The membrane separation method according to the invention can be adjusted in various ways in terms of control technology, depending on the respective controlled variable, an actuator present for influencing the controlled variable, and control priority. There are various controlled variables for the present method, such as the fill level of the feed vessel, the pressure on the retentate side and on the permeate side, the differential of which results in the transmembrane pressure (TMP), and the mass flow rates of retentate and permeate that can be influenced by various actuators, for example the conveying device or one or more adjustable flow resistors.

35 The membrane separation method according to the invention, in a preferred embodiment, is adjusted in terms of control technology in such a way that the mass flow rate of the retentate and the TMP are kept constant. These two parameters consequently have the highest control priorities, where the exact sequence of the control priorities can be fixed as desired, i.e. the mass flow rate of the retentate may have the highest control priority and the TMP the second highest control priority, or vice versa.

The mass flow rate of the feed to the (first) membrane module in the method according to the invention may be established in a manner known to the person skilled in the art, for example via the conveying device used for the (first) membrane stage. The exact embodiment for establishment of the mass flow rate of the feed to the (first) membrane stage is variable and usually depends on technical constraints, for example the type of pump chosen, the conveying rate and the conveying pressure. It would be possible to implement control of the feed mass flow rate, for example, with a pump controlled directly by means of speed, for example a gear pump, a piston pump, a piston membrane pump or optionally a multistage centrifugal pump. Another option for control of the feed mass flow rate may be that of using a centrifugal pump and an adjustable flow resistor, such as a (control) valve. A further option would be the use of a pump, for example a gear pump, a piston pump, a piston membrane pump or a centrifugal pump, in combination with an adjustable return flow conduit, for example from the pressure side to the suction side of the pump.

The pressure on the retentate side (retentate pressure) can be controlled by means of the conveying device and/or optionally a further actuator, for example a supply pressure regulator. The retentate pressure in the method according to the invention may be 1 to 100 bar, preferably 10 to 80 bar and more preferably 30 to 60 bar. The retentate pressure is here greater than the pressure on the permeate side (permeate pressure). The permeate pressure may here be 0 to 50 bar, preferably 0 to 10 bar and more preferably 1 to 5 bar. The permeate pressure in all membrane modules present, in a preferred embodiment, is similar (mutual variance of not more than 10%) or the same.

The transmembrane pressure formed by the differential of retentate pressure and permeate pressure may be 1 to 90 bar, preferably 10 to 80 and more preferably 30 to 60 bar. The membrane unit, or the individual membrane stages, preferably comprise(s) closed-loop control of the pressure on the retentate side, comprising at least the conveying device and a manometer, where the retentate pressure can be adjusted depending on the manometer. The retentate pressure here may be controlled by adjusting, for example, the conveying volume of the conveying device and optionally by means of a further actuator, for example a supply pressure regulator, depending on the retentate pressure measured (by the manometer), wherein – based on a target value fixed beforehand for the retentate pressure – the conveying volume of the conveying device is reduced when the retentate pressure is elevated and/or rising and the conveying volume of the conveying device is increased when the retentate pressure is reduced and/or falling.

The retentate pressure may alternatively be controlled via a combination of a manometer and an adjustable flow resistor, especially a valve on the retentate side. The retentate pressure can be controlled here, for example, via the valve setting, depending on the retentate pressure measured (by the manometer), wherein – based on a target value fixed beforehand for the retentate pressure

– the valve is opened further when the retentate pressure is elevated and/or rising and closed further when the retentate pressure is reduced and/or falling.

5 The mass flow rate of the retentate (retentate mass flow rate) in the method according to the invention is preferably controlled by means of a mass flow regulator on the retentate side, comprising at least one mass flow meter and an adjustable flow resistor, preferably a valve. The retentate mass flow rate can be controlled here by adjusting the mass flow regulator depending on the retentate mass flow rate measured, wherein – based on a target value fixed beforehand for the retentate mass flow rate – the valve of the mass flow regulator is closed further when the retentate
10 mass flow rate is elevated and/or rising and the valve of the mass flow regulator is opened further when the retentate mass flow rate is reduced and/or falling. The retentate pressure can then be chosen freely within the scope of the minimum necessary and maximum possible loading of the membrane stage(s).

15 In another embodiment, it is alternatively possible that the retentate mass flow rate is controlled by means of a combination of mass flow meter and the conveying device. The retentate mass flow rate can be controlled here, for example, by adjusting the conveying volume of the conveying device depending on the retentate mass flow rate measured, wherein – based on a target value fixed beforehand for the retentate mass flow rate – the conveying volume of the conveying device
20 is reduced when the retentate mass flow rate is elevated and/or rising and/or the conveying volume of the conveying device is increased when the retentate mass flow rate is reduced and/or falling.

The sensors and actuators for the closed-loop control of mass flow rate on the retentate side, comprising at least the conveying device or an adjustable flow resistor and a mass flow meter, and
25 the aforementioned closed-loop control of pressure on the retentate side, comprising at least the conveying device or an adjustable flow resistor and a manometer, may be connected to one another in any desired manner for control technology purposes, in order to control the two controlled variables of retentate mass flow rate and retentate pressure. The mutual priority of the two controlled variables of retentate mass flow rate and retentate pressure can be chosen as
30 desired in the method according to the invention. The priority of the two controlled variables of retentate mass flow rate and retentate pressure (and hence the TMP) is preferably higher than that of all other controlled variables in the membrane separation stage, i.e. has the fastest response characteristics.

35 The mass flow rate of the permeate removed (from the last membrane stage), depending directly or indirectly on the fill level of the feed vessel, is subject to preferably continuous closed-loop control, a feature of which is that – based on a target value fixed beforehand for the fill level of the feed vessel, where the target value is preferably 20% to 80%, more preferably 30% to 70%, of the maximum possible fill level – the mass flow rate of the permeate removed increases with rising fill

- level of the feed vessel and the mass flow rate of the permeate removed decreases with falling fill level of the feed vessel. In this type of closed-loop control, the feed vessel is not completely filled since the fill level is otherwise at or above the upper edge of its measurement range and hence is unknown, as a result of which no closed-loop control to a target value is possible. The mass flow rate of the permeate removed is especially adjusted via at least one adjustable flow resistor. In the case of continuous closed-loop control, this preferably keeps the fill level of the feed vessel constant. The effect of the closed-loop control principle according to the fill level of the feed vessel would be, for example, that, on attainment of a low level in the feed vessel, the mass flow rate of the permeate removed is reduced ever further and possibly no further permeate is removed.
- The temperature of the three streams of feed, retentate and permeate may vary within a wide range. The temperature of each of the three streams of feed, retentate and permeate is independently preferably -30°C to 150°C , more preferably 0°C to 100°C and most preferably 20°C to 80°C .
- A contribution to the achievement of the aforementioned modes of execution of the method according to the invention in terms of control technology is also made by the construction of the membrane unit, which is to be described in more detail hereinafter.
- The membrane unit which is used in the method according to the invention for separating the component from the mixture comprises at least one membrane stage. The membrane unit may alternatively comprise multiple membrane stages connected in series to one another. In this case, the overall permeate stream is divided only in the last membrane stage.
- A membrane stage of the membrane unit for the method according to the invention, according to the above definition, comprises a conveying device. The conveying device with which the mixture is guided as feed to the one or more membrane modules is preferably adjustable with regard to its conveying volume. The pressure of the feed to the one or more membrane modules may be 1 to 100 bar, preferably 10 to 80 bar and more preferably 30 to 60 bar. Suitable conveying devices are, for example, pumps known to the person skilled in the art, such as centrifugal pumps, piston pumps, piston membrane pumps, rotary piston pumps or gear pumps.
- A membrane stage of the membrane unit according to the invention further comprises one or more membrane module(s). There is theoretically no upper limit to the number of membrane modules; instead, it depends on the general process parameters and the desired membrane area. In a preferred embodiment, the membrane stage comprises multiple membrane modules that are further preferably connected in series to one another. The mixture arriving at the membrane unit is guided to the (first) membrane stage, where it is guided to the one or more membrane modules by means of the conveying device as feed. The separation into permeate and retentate is effected

within the membrane stage, with a permeate stream being withdrawn from each membrane module present.

5 In the case that there are multiple membrane modules, accordingly, a number of permeate streams corresponding to the number of membrane modules is generated. The membrane modules are preferably connected to one another on the permeate side, for example via a collecting rail. By contrast, however, especially in the case of series connection, only one retentate stream is obtained, since the retentate from the first membrane module is guided to the next membrane module, a further permeate is separated from the retentate, and the retentate from the second
10 membrane module is then guided to the next membrane module or, if there are only two membrane modules, it is conducted out of the membrane stage and/or the membrane unit.

A membrane stage in the method according to the invention comprises a feed vessel upstream of the conveying device, from which the feed is guided to the at least two membrane modules as feed
15 by means of the conveying device. If there is just one membrane stage, it is possible for both the feed to the membrane stage and the recycled permeate from the membrane stage to be introduced into the feed vessel and collected therein before they are guided by means of the conveying device as feed to the at least two membrane modules. If there is more than one membrane stage, the feed to the membrane stage and a retentate from one of the subsequent stages can be collected in the
20 feed vessel for the first stage, while the permeate from the respective preceding membrane stage and either the retentate from the subsequent stage or, in the last membrane stage, recycled permeate can be collected in the feed vessel for the subsequent stage(s). The construction and specifications of such a feed vessel are known to the person skilled in the art. The feed vessel preferably comprises a measurement unit for the fill level. It is also possible in both variants that the
25 respective recycled streams are guided not into the feed vessel but rather beyond the feed vessel but upstream of the conveying device.

The membrane stage may further comprise sensors and/or actuators in order to be able to fulfil the aforementioned, preferably control-related, functions. These especially include measurement
30 and/or control units for the parameters such as temperature, pressure, mass flow rate or the like. Corresponding measurement and control units are known to the person skilled in the art.

A membrane module according to the present invention, of which there may be one or more in the membrane stage, comprises one or more membrane element(s). In principle, membrane modules
35 may, as mentioned, be configured either as a membrane loop or as a membrane rack. The membrane modules present in accordance with the invention in the membrane stage(s) are preferably membrane loops.

A membrane loop comprises one or more membrane element(s) and at least one conveying device. A membrane loop preferably comprises just one conveying device. This conveying device is not identical to the conveying device for the corresponding membrane stage; instead, in that case, the entire system has at least two conveying devices. The conveying device of the
 5 membrane loop is generally responsible for the circulation of the membrane loop, while the conveying device of the membrane stage is generally responsible for the pressurization of the membrane modules or of the membrane loop. The conveying device used may be any suitable pump. Such pumps are known to the person skilled in the art. The pump used as conveying device within a membrane loop is preferably a centrifugal pump. The conveying device generates a
 10 moving overflow circulation. The overflow circulation can ideally improve mass transfer and hence the separation performance of the membrane. The overflow circulation can be adjusted here independently of the overriding control concept and the external and internal mass balance.

A membrane loop may additionally also comprise measurement and/or control units for parameters
 15 such as temperature, pressure differential (axial pressure drop), circulation rate or the like, for example a heater or cooler in order to adjust the temperature. Further measurement and control units are known to the person skilled in the art. In a preferred embodiment, the pressure in all membrane groups present in a membrane stage is similar (variance < 10%) or identical. This at least similar pressure can be established without the presence of a particular control unit, but may
 20 also be established by means of a pressure regulator. The pressure regulator for the permeate pressure preferably has the slowest response characteristics compared to the other actuators, i.e. the closed-loop control of mass flow on the permeate side, the closed-loop control of mass flow on the retentate side and the closed-loop control of pressure on the retentate side.

25 By contrast with the above-described membrane loop, a membrane module configured as a membrane rack does not have a conveying device, but rather one or more membrane elements and optionally additional measurement and control units.

The membrane element(s) present in the membrane module, preferably in the membrane loop, are
 30 elements prefabricated for industrial use that contain the membrane and can be considered as a base unit that cannot be divided any further in the membrane separation method according to the invention. The membrane element(s) may be used as such in the membrane module or be disposed in a pressure housing, for example a pressure tube. The pressure tube considered in isolation may contain one or more membrane element(s), preferably up to five membrane
 35 elements. If the membrane element(s) are disposed in a pressure housing, preferably a pressure tube, a membrane module may comprise multiple pressure tubes. The flow preferably passes in series on the feed or retentate side through the membrane elements disposed in a pressure tube, and they are preferably connected on the permeate side. Base units used as membrane element

may be spiral-wound elements known to the person skilled in the art. One or more spiral-wound elements may then be present in a pressure housing, preferably a pressure tube.

Membranes used are preferably those having a separation-active layer made of a material selected
 5 from the group consisting of cellulose acetate, cellulose triacetate, cellulose nitrate, regenerated cellulose, polyimides, polyamides, polyetheretherketones, sulfonated polyetheretherketones, aromatic polyamides, polyamidoimides, polybenzimidazoles, polybenzimidazolones, polyacrylonitrile, polyarylethersulfones, polyesters, polycarbonates, polytetrafluorethylene, polyvinylidene fluoride, polypropylene, terminally or laterally organomodified siloxane,
 10 polydimethylsiloxane, silicones, silicone acrylates, polyphosphazenes, polyphenylsulfides, polybenzimidazoles, Nylon® (nylon-6,6), polysulfones, polyanilines, polypropylenes, polyurethanes, acrylonitrile/glycidyl methacrylate (PANGMA), polytrimethylsilylpropynes, polymethylpentynes, polyvinyltrimethylsilane, polyphenylene oxide, alpha-aluminium oxides, gamma-aluminium oxides, titanium oxides, silicon oxides, zirconium oxides, ceramic membranes hydrophobicized with
 15 silanes, as described in EP 1 603 663 B1, polymers with intrinsic microporosity (PIM) such as PIM-1 and others, as described, for example, in EP 0 781 166 B1, or mixtures thereof. The abovementioned substances may be in crosslinked form in the separation-active layer through addition of auxiliaries, or in the form of what are called mixed matrix membranes with fillers, for example carbon nanotubes, metal-organic frameworks or hollow spheres, and particles of inorganic
 20 oxides or inorganic fibres, for example ceramic fibres or glass fibres.

Particular preference is given to using membranes having, as a separation-active layer, a polymer layer of terminally or laterally organomodified siloxane, polydimethylsiloxane, silicone acrylates or polyimide, formed from polymers having intrinsic microporosity (PIM) such as PIM-1, or wherein the
 25 separation-active layer has been formed by means of a hydrophobized ceramic membrane. Very particular preference is given to using membranes formed from terminally or laterally organomodified siloxanes or polydimethylsiloxanes. Membranes of this kind are commercially available.

30 As well as the abovementioned materials, the membranes may include further materials. More particularly, the membranes may include support or carrier materials to which the separation-active layer has been applied. A selection of support materials is described by EP 0 781 166, to which reference is made explicitly.

35 In a particularly preferred embodiment, the method described is utilized for membrane separation of a homogeneous catalyst. The component to be separated off is then the homogeneous catalyst, and the liquid mixture is the reaction mixture obtained from a reaction stage.

A particularly preferred method according to the present invention is therefore a method of continuously separating a homogeneous catalyst from a liquid reaction mixture using a membrane unit which comprises at least one membrane stage and is fed with the reaction mixture containing the homogeneous catalyst and coming from a reaction zone as feed,

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wherein a membrane stage consists at least of a conveying device, one or more membrane module(s) and a feed vessel upstream of the conveying device, and wherein the reaction mixture is guided from the feed vessel by means of the conveying device as feed to the one or more membrane modules, which results in reduction of the homogeneous catalyst, based in each case on the reaction mixture guided to the respective membrane module, in the resulting permeate stream and enrichment in the resulting retentate stream, characterized in that

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the overall permeate stream obtained is divided and a portion of the overall permeate stream, the recycled permeate, is recycled to the feed vessel and/or beyond the feed vessel but upstream of the conveying device and the other portion of the overall permeate stream, the permeate removed, is conducted out of the at least one membrane stage and out of the membrane unit on the permeate side.

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The reaction mixture comes from a reaction zone suitable for the respective method, preferably one or more suitable reactors. The retentate stream containing at least a majority of the homogeneous catalyst is preferably recycled to the reaction zone, especially the reactor(s), optionally after prior purification and/or workup of the catalyst. Since the mass flow rate from the reaction zone can vary for production-related reasons, the above-described control- and plant-related functions can also be employed in the separating-off of homogeneous catalysts.

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In the reaction zone, preferably the reactor(s), a homogeneously catalysed reaction is accordingly conducted. These reactions may be the following: oxidations, epoxidations, hydroformylations, hydroaminations, hydroaminomethylations, hydrocyanations, hydrocarboxylations, hydrocarbonylations, hydrocarboxyalkylations, alkoxycarbonylations, aminations, ammoxidation, oximinations, hydrosilylations, ethoxylations, propoxylations, carbonylations, telomerizations, metatheses, Suzuki couplings and hydrogenations.

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Preference is given to a hydroformylation. The hydroformylation is especially a hydroformylation of olefins having 3 to 15 carbon atoms, preferably 8 to 12 carbon atoms. The hydroformylation is preferably a homogeneously catalysed hydroformylation in which the catalyst system is (fully) dissolved in the liquid phase of the reaction mixture. The catalyst system for the hydroformylation preferably comprises a transition metal from group 8 or 9 of the Periodic Table of the Elements (PTE) and at least one organic phosphorus-containing ligand. Suitable phosphorus-containing

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ligands are known to the person skilled in the art, but are preferably monodentate phosphorus-containing ligands, for example tris(2,4-di-tert-butylphenyl)phosphite.

Transition metals used may especially be iron, ruthenium, iridium, cobalt or rhodium, preferably
 5 cobalt or rhodium, more preferably rhodium. Catalytically active species discussed are typically (ligand)-carbonyl complexes of the metal atoms that form in the liquid reaction mixture under elevated pressure and elevated temperature.

The hydroformylation may be conducted in the presence of a solvent, in which case the solvent
 10 should be compatible with the hydroformylation method. Solvents used may be suitable solvents known to the person skilled in the art for hydroformylation, for example alkanes, aromatic hydrocarbons, water, ethers, esters, ketones, alcohols and the reaction products or by-products of the hydroformylation, such as aldehydes and condensation products of the aldehydes.

15 In addition, the hydroformylation can be conducted at a pressure of 10 to 400 bar, preferably 15 to 270 bar. The temperature in the hydroformylation may be 70 to 250°C, preferably 100 to 200°C, more preferably 120 to 160°C.

The present invention is described by the figures which follow, in which particular embodiments are
 20 shown. The figures constitute merely an illustration and should not be regarded as limiting.

Fig. 1 shows an illustrative construction of a membrane unit comprising one membrane stage. A membrane stage consists here of a feed vessel (B-1), a pump (P-1) and a membrane module (M-1). The feed vessel (B-1) is fed with the liquid mixture as feed to the membrane stage (F-1). From
 25 the feed vessel (B-1), the liquid mixture is guided by the pump (P-1) as feed (F-2) to the membrane module (M-1), for example a membrane loop, where the actual membrane separation takes place. From the membrane module (M-1), the retentate (F-3) via the discharge valve (V-1) and the overall permeate (F-4) are then withdrawn. The overall permeate (F-4) is subsequently divided, by means of which a portion of the overall permeate can be removed (F-5) via the discharge valve (V-2) from
 30 the membrane stage and the membrane unit, and the other portion of the permeate (F-6) recycled to the feed vessel (B-1) via the recycling valve (V-3).

Fig. 2 shows an illustrative construction of a membrane unit comprising one membrane stage but multiple membrane modules. A membrane stage consists of a feed vessel (B-1), a pump (P-1) and
 35 two membrane modules (M-1/M-2). The feed vessel (B-1) is fed with the liquid mixture as feed to the membrane stage (F-1). From the feed vessel (B-1), the liquid mixture is guided by the pump (P-1) as feed (F-2) to the first membrane module (M-1), for example a membrane loop, where the first membrane separation in this case takes place. From the membrane module (M-1), the retentate from the first membrane module (F-3) and the permeate from the first membrane module (F-4) are

then withdrawn. The retentate (F-3) is guided to the second membrane module (M-2), where a further membrane separation takes place, which gives rise to the permeate (F-8) and the retentate (F-7) from the second membrane module (M-2). The retentate (F-7) is withdrawn via the discharge valve (V-1). The two permeates (F-4/F-8) from the two membrane modules (M-1/M-2) are
 5 combined to give an overall permeate (F-14) and then divided, as a result of which a portion of the overall permeate (F-5) can be removed via the discharge valve (V-2) and the other portion of the permeate (F-6) can be recycled to the feed vessel (B-1) via the recycling valve (V-3).

Fig. 3 shows an illustrative construction of a membrane unit comprising two membrane stages. The
 10 membrane stages each consist of a feed vessel (B-1/B-2), a pump in each case (P-1/P-2) and a membrane module (M-1/M-2). The feed vessel (B-1) is fed with the liquid mixture as feed to the membrane stage (F-1). From the feed vessel (B-1), the liquid mixture is guided by the pump (P-1) as feed (F-2) to the membrane module (M-1), for example a membrane loop, where the membrane separation takes place. From the membrane module (M-1), the overall permeate (F-4) from the first
 15 membrane stage and the retentate (F-3) are then withdrawn via the discharge valve (V-1). The permeate (F-4) from the first membrane module (M-1) is guided to the feed vessel (B-2) for the second membrane stage and thence guided by means of a pump (P-2) as feed (F-9) to the membrane module (M-2) of the second membrane stage (M-2), where a further membrane separation takes place. From the membrane module (M-2) of the second membrane stage, the
 20 overall permeate (F-11) from the second membrane stage (M-2) and the retentate (F-10) are removed. The retentate (F-10) is subsequently guided via the discharge valve (V-4) to the feed vessel (B-1) of the first membrane stage. The overall permeate (F-11) is divided after exiting from the membrane module (M-2), as a result of which a portion of the permeate (F-12) can be removed via the discharge valve (V-5) and the other portion of the permeate (F-13) can be recycled to the
 25 feed vessel (B-2) of the second membrane stage (M-2) via the recycling valve (V-6).

Fig. 4 corresponds fundamentally to Fig. 1, i.e. contains just one membrane stage, but contains additional markings for illustration of the mass balances addressed. The term "mass balance" in the present application is used on the basis of two fundamental assumptions. The first relevant
 30 assumption is that the system is a steady-state system, which means in the present case that no accumulation of the mixtures of matter takes place within the membrane unit over time, but there can be temporary fluctuations at most. The total mass in the system thus remains the same irrespective of time. At the same time, which is the second assumption, no reaction takes place in our mass balance circuit. This means that not just the total mass but also the masses of the
 35 individual components remain the same.

The external overall mass balance is based on the dotted marking in Fig. 4. The mass flow of the feed F-1 is equal to the sum total of the mass flow of the retentate F-3 and of the mass flow of the permeate F-5, i.e. $F-1 = F-3 + F-5$.

The internal overall mass balance based on the box with twin dotted lines around the membrane stage M-1 in Fig. 4 is defined correspondingly: The mass flow of the feed F-2 is equal to the sum total of the mass flow of the retentate F-3 and of the mass flow of the overall permeate F-4, i.e. F-2 = F-3 + F-4.

It follows that, in the case of specification of two streams of the external mass balance, it is the third stream that results in the external mass balance. It is thus possible to determine just two of the three streams independently, or controlled from the outside. The situation is just the same for the internal mass balance, although it should be noted here that the external mass balance always defines at least one stream of the internal mass balance. Accordingly, it is possible overall to fix just two streams of the external mass balance and one additional stream of the internal mass balance. All other streams result therefrom.

Claims

1. Method of continuously separating a component from a liquid mixture using a membrane unit which comprises at least one membrane stage and is fed with the mixture as feed,
 5 wherein a membrane stage consists at least of a conveying device, one or more membrane module(s) and a feed vessel upstream of the conveying device, and wherein the mixture is guided from the feed vessel by means of the conveying device as feed to the one or more membrane modules, which results in reduction of the component to be separated off, based
 10 in each case on the mixture guided to the respective membrane module, in the resulting permeate stream from this respective membrane module and enrichment in the resulting retentate stream from this respective membrane module or vice versa, characterized in that
 15 the overall permeate stream obtained from the last membrane stage is divided and a portion of the overall permeate stream, the recycled permeate, is recycled to the feed vessel and/or beyond the feed vessel but upstream of the conveying device and the other portion of the overall permeate stream, the permeate removed, is conducted out of the last membrane stage and out of the membrane unit on the permeate side, wherein the recycling of the recycled permeate to the feed vessel and/or beyond the feed vessel but upstream of the
 20 conveying device is effected not by means of a conveying device but by hydraulic means, i.e. by means of a pressure differential that exists between the permeate side of the membrane unit and the suction side of the conveying device or the feed vessel.
2. Method according to Claim 1, wherein the mass flow rate of one of the three streams
 25 selected from feed to the membrane unit, the permeate removed, and the retentate from the membrane unit is applied to a preceding or downstream process step, and one further stream of the three is controlled toward a target value.
3. Method according to any of the preceding claims, wherein the mass flow rate of the
 30 permeate recycled can fluctuate and is established depending on the mass flow rate of the permeate removed.
4. Method according to any of the preceding claims, wherein the pressure on the retentate side and/or the pressure on the permeate side or the resulting transmembrane pressure (TMP)
 35 and optionally the membrane module temperature are controlled in order to obtain a desired amount of the overall permeate stream.

5. Method according to any of the preceding claims, wherein both the mass flow rate of the permeate removed and the permeate pressure are controlled by means of an adjustable flow resistor.
- 5 6. Method according to any of the preceding claims, wherein the mass flow rate of the permeate removed, depending directly or indirectly on the fill level of the feed vessel, is subject to preferably continuous closed-loop control, a feature of which is that – based on a target value fixed beforehand for the fill level of the feed vessel – the mass flow rate of the permeate removed increases with rising fill level of the feed vessel and the mass flow rate of
10 the permeate removed decreases with falling fill level of the feed vessel.
7. Method according to any of the preceding claims, wherein the pressure on the retentate side (retentate pressure) is controlled by means of the conveying device with which the feed is fed to the one or more membrane modules, and optionally a further actuator, for example a
15 supply pressure regulator, or by means of a combination of a manometer and an adjustable flow resistor, especially a valve on the retentate side.
8. Method according to any of the preceding claims, wherein the mass flow rate on the retentate side (retentate mass flow rate) is controlled by means of a closed-loop mass flow
20 controller on the retentate side comprising at least a mass flow meter and an adjustable flow resistor, preferably a valve, or by means of a combination of mass flow meter and conveying device.
9. Method according to any of the preceding claims, wherein the component is a homogeneous
25 catalyst which is separated from a reaction mixture.
10. Method according to any of the preceding claims, wherein the conveying device is a pump.
11. Method of continuously separating a homogeneous catalyst from a liquid reaction mixture
30 using a membrane unit which comprises at least one membrane stage and is fed with the reaction mixture containing the homogeneous catalyst and coming from a reaction zone as feed,

wherein a membrane stage consists at least of a conveying device, one or more membrane
35 module(s) and a feed vessel upstream of the conveying device, and wherein the reaction mixture is guided from the feed vessel by means of the conveying device as feed to the one or more membrane modules, which results in reduction of the homogeneous catalyst, based in each case on the reaction mixture guided to the respective membrane module, in the

resulting permeate stream and enrichment in the resulting retentate stream, characterized in that

5 the overall permeate stream obtained is divided and a portion of the overall permeate stream, the recycled permeate, is recycled to the feed vessel and/or beyond the feed vessel but upstream of the conveying device and the other portion of the overall permeate stream, the permeate removed, is conducted out of the at least one membrane stage and out of the membrane unit on the permeate side.

10 12. Method according to Claim 11, wherein the reaction mixture is taken from a reaction zone in which a homogeneously catalysed reaction is being conducted.

13. Method according to Claim 12, wherein the homogeneously catalysed reaction is selected from the group of the following reactions: oxidations, epoxidations, hydroformylations,
15 hydroaminations, hydroaminomethylations, hydrocyanations, hydrocarboxylations, hydrocarbonylations, hydrocarboxyalkylations, alkoxycarbonylations, aminations, ammoxidation, oximations, hydrosilylations, ethoxylations, propoxylations, carbonylations, telomerizations, metatheses, Suzuki couplings and hydrogenations.

20 14. Method according to Claim 13, wherein the homogeneously catalysed reaction is a hydroformylation.